

**VOLATILE ORGANIC COMPOUNDS (VOCs) in Ambient Air
Using Summa Canister Sampling and Gas Chromatography (GC) Analysis**

Table 1A. Summary of Holding Times and Preservation

Analytical Parameter ^a	Technical and Contract Holding Times	Preservation
Volatile Organic Compounds (VOCs) in SUMMA® canisters ^b	<u>Technical</u> : 14 days from collection; <u>Contract</u> : 12 days from receipt at laboratory	Ambient temperature; near atmospheric pres
VOCs in tedlar bags	<u>Technical</u> : 48 hours from collection; <u>Contract</u> : 36 hours from receipt at laboratory	Ambient temperature; near atmospheric pres

^a Individual target compounds are listed in Table 1B.

^b The laboratory must provide clean and certified 6-liter SUMMA® canisters with the manufacturer's serial number, or a unique permanent identification number attached. For cleaning and certification of SUMMA® canisters, follow the requirements specified in Sections 7.3 and 11 of EPA Method TO-14. After cleaning and certification, the SUMMA canisters will be shipped to the field with a vacuum of < 50 mm TORR. One canister shall be designated as the trip blank for each SDG.

Data Calculations and Reporting Units:

Calculate and report the sample results as specified in the EPA Method TO-14. Perform sample quantitation using the response factor (RF) from the average response factors of the calibrated range. Report results for all target analytes in concentration units of parts per billion by volume (ppbv).

Report tentatively identified compounds (TICs) with a response of <10% of the nearest internal standard.

TIC values should be estimated in ppbv based on the response of the corresponding internal standard.

Table 1B. Target Compound List and Contract Required Quantitation Limits for VOCs by EPA Method TO-14

<u>Analyte</u>	<u>CAS Numbers</u>	<u>CRQL(ppbv)</u>
Acetone	67-64-1	5
Acetonitrile	27521	5
Acrolein	39120	5
Acrylonitrile	39447	5
Benzene	71-73-2	2
Benzyl chloride	100-44-7	5
Bromodichloromethane	75-27-4	2
Bromomethane	74-83-9	5
1,3-Butadiene	106-99-0	5
2-Butanone	78-87-5	5
Carbon tetrachloride	56-32-5	2
Chlorobenzene	108-90-7	2
Chlorodifluoromethane		2
Chloroethane	0	2
Chloroform	67-66-3	2
Chloromethane	74-87-3	2
3-Chloro-1-propene		2
Cyclohexane	110-82-7	2
Dibromochloromethane	124-48-1	2
1,2-Dibromoethane	106-93-4	2
1,2-Dichlorobenzene	95-50-1	2
1,3-Dichlorobenzene	541-73-1	5
1,4-Dichlorobenzene	106-46-7	5
Dichlorodifluoromethane	75-71-8	2
1,1-Dichloroethane	75-34-3	2
1,2-Dichloroethane	39234	2
1,1-Dichloroethene	75-35-4	5
cis-1,2-Dichloroethene	156-59-2	2

trans-1,2-Dichloroethene	156-60-5	2
1,2-Dichloropropane	78-87-5	2
Dichlorofluoromethane	75-43-4	2
t-1,2-Dichloropropene		2
cis-1,2-Dichloropropene		5
1,2-Dichloro-1,1,2,2-tetrafluoroethane		2
Ethylbenzene	100-41-4	2
Heptane	142-82-5	2
Hexachlorobutadiene	87-68-3	5
Hexane	110-54-3	2
Methanol	67-56-1	5
Methylene chloride	27638	5
Methyl methacrylate		2
4-Methyl-2-pentanone	39721	5
alpha-Methyl styrene		5
Octane	111-65-9	5
n-Pentane	109-66-0	2
Propylene	42185	5
Styrene	100-42-5	5
1,2,4-Trichlorobenzene	120-82-1	2
1,1,1-Trichloroethane	71-55-6	5
1,1,2-Trichloroethane	0	5
1,1,2,2-Tetrachloroethane	79-34-5	2
Tetrachloroethene	127-18-4	5
Toluene	108-88-3	5
Trichloroethene	28860	2
Trichlorofluoromethane	75-69-4	2
1,1,2-Trichloro-1,2,2-trifluoroethane		2
1,2,4-Trimethylbenzene	95-63-6	2
1,3,5-Trimethylbenzene	108-67-8	2
Vinyl acetate	39571	5
Vinyl chloride	27397	2

Xylenes (m- and p-)		5
Xylene (o-)		5

Table 2. Summary of Calibration Procedures

Calibration Element	Frequency	Acceptance Criteria	Correctiv
GC/MS Tuning with 4-bromofluorobenzene (BFB)	Beginning of each 12 hour period during which standards and samples are analyzed	Ion abundance criteria in Table 4 of Method TO-14	1. Identifi 2. MS tur met befor
Initial Calibration (minimum blank + 3 to 5 points for each analyte) (ICAL) ^{a, b, c}	Initially; whenever required, due to failure of CCV	RSD for RFs #25%	1. Termin 2. Recali before sa
Continuing Calibration Verification (CCV) (middle of the calibration range)	Following ICV, after every 10 samples, and end of run	%D between RF of CCV and avg. RRFs from ICAL #25%	1. Recali 2. Reanal last good

^a The ICAL low standard must be at concentrations equivalent to the CRQL.

^b ICAL and CCV standards must contain all target analytes listed in Table 1B.

^c Report the retention time (RT) window for each analyte. Determine RT windows as $\pm 3 \times$ the standard deviation (SD) of the average initial calibration RT for each analyte.

Follow the tuning and calibration procedures in Section 10.2.2 and 10.2.3 of EPA Method TO-14 and in SOP #1705, Section 3.7.1 and 3.7.2 of OSWER Directive 9360.4-05, May 1992.

The standards must be traceable to a known certified source.

Table 3. Summary of Internal Quality Control Procedures

QC Element	Frequency	Acceptance Criteria	Corrective
Method Blank (MB)	One for each day, minimum of one per SDG	< CRQL for each compound	1. Investig contaminati 2. Reanalyz processed w out of cont
Performance Evaluation (PE) sample ^a	One per day or for each SDG batch	80-120% of expected value	1. Reanalyz associated compliant P
Surrogate Spikes ^b	Every sample, standard and method blank	70-130% of expected value	1. Reanalyz non-complia recoveries.
Laboratory Duplicates	One of every 10 samples or one per day, whichever is greater	RPD #20 between duplicate results \$5 times CRQL; ±CRQL for duplicate results #5 times CRQL	1. Reanalyz non-complia

^a PE samples - The National Institute of Standards and Technology (NIST) standard reference materials (SRM) that are traceable to known concentrations.

^b Surrogates - The laboratory must demonstrate that the selected three surrogates do not interfere with any target analytes.

Dilute and reanalyze samples which contain one or more target analytes at concentrations above the initial calibration range. Results for such reanalyses should fall within the mid-range of the calibration curve. Report results and submit documentation for both analyses.

VOLATILE ORGANIC COMPOUNDS (VOCs) in Air
(Ambient Air/Soil Vapor/Stack Gas) Samples Collected in Specially-Prepared
Canisters
and Analyzed by Gas Chromatography/Mass Spectrometry (GC/MS)

Table 1A. Summary of Holding Times and Preservation

Analytical Parameter ^a	Technical and Contract Holding Times	Preservation
Volatile Organic Compounds (VOCs) in SUMMA® canisters ^b	<u>Technical</u> : 14 days from collection; <u>Contract</u> : 10 days from receipt at laboratory	Ambient tempera
VOCs in tedlar bags	<u>Technical</u> : 48 hours from collection; <u>Contract</u> : 36 hours from receipt at laboratory	Ambient tempera

^a Individual target compounds are listed in Table 1B.

^b The laboratory must provide the following equipment certified as clean:

Cleaned and evacuated 6-liter SUMMA® canisters with the manufacturer's serial number, or a unique permanent identification number attached. For cleaning and certification of SUMMA® canisters, follow the requirements specified in Section 8.4 of EPA Method TO-15 (January 1999).

Cleaned and preset ultra-low flow orifices for each ambient air sample preset by the laboratory at a flow rate of 3.2 mL/min ±10% and digital flow meters capable of accurate measurements in the 3.2 mL/min range.

Leak test all canisters prior to sample collection according to Section 8.4 of Method TO-15 (January 1999).

Data Calculations and Reporting Units:

Calculate and report the sample results as specified in Section 10.8.4 of EPA Method TO-15 (January 1999).

EPA Method TO-15 (January 1999)

Perform sample quantitation using the relative response factor (RRF) from the daily continuing calibration standard. Report results for all target analytes in concentration units of parts per billion by volume (ppbv). Report tentatively identified compounds (TICs) with a response of <10% of the nearest internal standard. TIC values should be estimated in ppbv based on the response of the corresponding internal standard.

EPA Method TO-15 (January 1999)

Table 1B. Target Compound List, CAS Numbers, and Contract Required Quantitation Limits

Analyte	CAS Number	CRQL	CRQL	CRQL	MDL
		ppbv	ug/M3	ug/L	ppbv
Benzene	71-43-2	1.0	3.5	0.0035	0.2
Bromomethane	74-83-9	1.0	4.2	0.0042	0.2
Carbon Tetrachloride	56-23-5	1.0	6.9	0.0069	0.2
Chlorobenzene	108-90-7	1.0	5.0	0.0050	0.2
Chloroethane	75-00-3	1.0	2.9	0.0029	0.2
Chloroform	67-66-3	1	5.3	0.0053	0.2
Chloromethane	74-87-3	1	2.3	0.0023	0.2
1,1-Dichloroethane	75-34-3	1	4.4	0.0044	0.2
1,2-Dichloroethane	107-06-2	1	4.4	0.0044	0.2
1,1-Dichloroethene	75-35-4	1.0	4.3	0.0043	0.2
cis-1,2-Dichloroethene	156-59-2	1.0	4.3	0.0043	0.2
trans-1,2-Dichloroethene	156-60-5	1.0	4.3	0.0043	0.2
1,2-Dichloropropane	78-87-5	1.0	5.0	0.0050	0.2
cis-1,3-Dichloropropene	10061-01-5	1.0	5.0	0.0050	0.2
trans-1,3-Dichloropropene	10061-02-6	1.0	5.0	0.0050	0.2
Ethylbenzene	100-41-4	1.0	4.7	0.0047	0.2
Methylene Chloride	75-09-2	1.0	3.8	0.0038	0.2
Styrene	100-42-5	1.0	4.6	0.0046	0.2
1,1,2,2-Tetrachloroethane	79-34-5	1.0	7.5	0.0075	0.2
Tetrachloroethene	127-18-4	1.0	7.4	0.0074	0.2
Toluene	108-88-3	1.0	4.1	0.0041	0.2
1,1,1-Trichloroethane (TCA)	71-55-6	1	6.0	0.0060	0.2
1,1,2-Trichloroethane	79-00-5	1	6	0.0060	0.2
Trichloroethene (TCE)	79-01-6	1.0	5.9	0.0059	0.2
Vinyl Chloride	75-01-4	1.0	2.8	0.0028	0.2
p-Xylene & m-Xylene	106-42-3 & 108-38-3	2.0	9.5	0.0095	0.4
o-Xylene	95-47-6	1.0	4.7	0.0047	0.2

EPA Method TO-15 (January 1999)

Table 2. Summary of Calibration Procedures

Calibration Element	Frequency	Acceptance Criteria	Correctiv
GC/MS Tuning with 4-bromofluorobenzene (BFB)	Beginning of each 12 hour period during which standards and samples are analyzed	Ion abundance criteria in Table 3 of Method TO-15	1. Identi 2. MS tur met befor
Initial Calibration (minimum blank + 5 points for each analyte) (ICAL) ^{a, b, c}	Initially; whenever required, due to failure of CCV	RRFs \$0.05 for each analyte; RSD for RRFs #30%	1. Termir 2. Recali before sa

Continuing Calibration Verification (CCV) (middle of the calibration range)	Following ICV, every 12-hour, and end of run	RRFs \$0.05 for each analyte; %D between RRF of CCV and avg. RRFs from ICAL #30%	1. Recali 2. Reanal last good
CRQL standard	Every 12 hour	65-135% of the expected value	1. Recali 2. Reanal last good
Internal Standards ^d	Every standard, sample, blank, and QC sample	IS area within ±40% of the IS area in the associated CCV	1. Invest 2. Re-ana analyzed malfunci
Retention time evaluation	Each analysis	±0.50 minute of the IS retention time in the associated CCV	1. Re-cal 2. Re-ana to last g

^a The ICAL low standard must be at concentrations equivalent to the CRQL.

^b ICAL and CCV standards must contain all target analytes listed in Table 1B.

^c Report the retention time (RT) window for each analyte. Determine RT windows as ±3 x the standard deviation (SD) of the average initial calibration RT for each analyte.

^d Internal standards: Bromochloromethane, 1,4-Difluorobenzene, and Chlorobenzene-d5. The standards must be traceable to known certified source. Humidify calibration standards when used.

EPA Method TO-15 (January 1999)

Table 3. Summary of Internal Quality Control Procedures

QC Element	Frequency	Acceptance Criteria	Corrective
Method Blank (MB)	Each 12-hour time period, minimum of one per SDG	< CRQL for each compound	1. Investig contaminati 2. Reanalyz processed w out of cont
Blank Spike Blank Spike Duplicate (BS/BSD)	One BS/BSD set per batch or SDG (1 MS/MSD set per 20 samples minimum)	65-135% of expected value; #35% RPD between BS and BSD	1. Report i
Surrogate Spikes ^a	Every sample, standard and method blank	80-120% of expected value	1. Reanalyz non-complia recoveries
Laboratory Duplicates	One per SDG	RPD #20 between duplicate results \$5 times CRQL; ±CRQL for duplicate results #5 times CRQL	1. Reanalyz non-complia

^a 1,2-dichloroethane-d₄, Toluene-d₈, and 4-Bromofluorobenzene. If other surrogates are used the laboratory must demonstrate that the surrogates do not interfere with any target analytes. The laboratory must also notify the Region in advance.

Reanalyze samples containing target analytes at concentrations greater than the initial calibration range. Analyze a smaller aliquot of sample from the SUMMA® canister. If after analyzing a smaller aliquot, the concentration is still greater than the initial calibration range, then dilute the sample and reanalyze according to

procedures outlined in EPA Method TO-15. If sample dilution is necessary, the dilution must be adjusted so that the target analyte is quantitated at a level in the upper half of the calibration range. Report the results and submit documentation for the analysis of both the diluted and undiluted sample.

Both the primary ions and the secondary ions must be present in the spectra. The acceptance level for relative abundance of the appropriate ions in all standards, method blanks, QC samples, laboratory duplicates and field samples is determined to be $\pm 20\%$ of the expected abundance observed in the most recent continuing calibration standard. All ions greater than 15% in the standard spectrum must be present in the sample spectrum.